

LA-UR-18-28626

Approved for public release; distribution is unlimited.

Title: Effect of a density dependent partition function on the EOS properties of neutral nitrogen and the doubly-ionized argon plasma

Author(s): Gammel, William Pierre
Leiding, Jeffery Allen

Intended for: Report

Issued: 2018-09-10

Disclaimer:

Los Alamos National Laboratory, an affirmative action/equal opportunity employer, is operated by the Los Alamos National Security, LLC for the National Nuclear Security Administration of the U.S. Department of Energy under contract DE-AC52-06NA25396. By approving this article, the publisher recognizes that the U.S. Government retains nonexclusive, royalty-free license to publish or reproduce the published form of this contribution, or to allow others to do so, for U.S. Government purposes. Los Alamos National Laboratory requests that the publisher identify this article as work performed under the auspices of the U.S. Department of Energy. Los Alamos National Laboratory strongly supports academic freedom and a researcher's right to publish; as an institution, however, the Laboratory does not endorse the viewpoint of a publication or guarantee its technical correctness.

Effect of a density dependent partition function on the EOS properties of neutral nitrogen and the doubly-ionized argon plasma

William P. Gammel and Jeffery A. Leiding
Theoretical Division, T-1
Los Alamos National Laboratory

I. INTRODUCTION

There have been many attempts^{1,2} to improve upon the calculation of the thermodynamic properties of plasmas. These properties are dependent on the form of the partition function, and so a study of these properties without a discussion of the partition function would be incomplete. Many previous authors have shown reasonable concern over the electronic contribution to the partition function, since it is well known that the series expression diverges. To remedy this, various authors have proposed techniques to truncate the divergent series in a physically meaningful way. Furthermore, the ionization potential in a plasma is lowered, which lowers the amount of energy a particle needs to become ionized. In plasmas, which consist of excited neutral particles, ions, and electrons, introducing a cutoff both restricts the internal partition function, as well as provides a measurable criterion for when the electron is considered no longer bound to the nucleus.

A few methods³⁻⁵ have introduced such a cutoff criterion. With the exception of the occupation probability formalism⁵, the most widely adopted models for the truncation of the internal partition function suppress all orbital radii that exceed a pre-determined distance. In this work we have first considered a model similar to Bond's³, where the radii of the hydrogen-like electron orbitals are determined by the Bohr radius, a_0 and the principle quantum number n . Explicitly, $a_n = a_0 n^2$. We then present what we believe to be a more mathematically rigorous version of this method, which uses the radial distribution function of the electron orbitals to determine the most probable value of a_n .

These methods have been used to calculate the thermodynamic properties of the nitrogen ideal gas and of the doubly-ionized ideal argon plasma. The doubly-ionized argon plasma was simplified significantly by assuming hydrogen-like states. We have elaborated on the validity of this reduction in Section II A. It is the author's opinion that a similar reduction cannot be applied to neutral nitrogen nor its cations, N^+ and N^{2+} , due to the nature of their low-lying quantum states. Therefore, similar calculations for the doubly-ionized nitrogen plasma have proven more challenging. Using the analytic form of the radial wave function given by Hibbert et al.⁶ we were able to extend our approach to neutral nitrogen.

The purpose of this work was to begin to explore various partition function truncation techniques in MAGPIE. Future work is expected to include wave functions for

the nitrogen cations as well as implementations of more advanced techniques such as the occupation probability formalism.⁵

II. PARTITION FUNCTION TRUNCATION METHODS

The internal partition function of a particle is given by

$$Z(T)_{elec} = \sum_j g_j e^{-E_j/kT} \quad (1)$$

where g_j is the degeneracy of the level and E_j is the energy that corresponds with quantum state j . In the case of hydrogen the degeneracy is equivalent to the square of the principle quantum number, and consequently causes the series to diverge. More intuitively, the partition function should be dependent upon volume, but the wavefunctions of hydrogen extend *ad infinitum*, making it impossible to contain them within a finite volume. Furthermore, the wavefunctions need to be contained within the volume occupied by a single particle so they do not overlap with quantum states of neighboring atoms. Thus a cutoff for the internal partition function is needed.

Many different methods for choosing this value have been proposed. Previous authors have used methods as simple as terminating the series after the ground state⁷, to more complex methods such as the occupation probability formalism⁵. We first consider a method that is only a slight modification to the approach found in Bond's work.

A. Bohr Radius Method

Both methods presented in this paper rely on the assumption that argon and its cations are hydrogen-like, and so it is crucial that we elaborate upon the validity of this assumption. It is well known that the energy of a hydrogen-like atom depends on the principle quantum number and the Rydberg energy. Explicitly, $E_n = -Ry/n^2$, where $Ry = 13.605$ eV. Thus, in the absence of fine and hyperfine structure, each principle quantum number n of an idealized hydrogen-like atom should correspond to a unique energy level. Since fine and hyperfine structure cannot be ignored, we expect a hydrogen-like atom to have near identical energy levels associated with each principle quantum number.

Futhermore, we note that if a model considers a third row species as hydrogenic, then its ground state principle quantum number transforms from $n = 3$ to $n = 1$. Broadly speaking, there is a mapping between the model n and the experimental n such that $n_{model} = n_{exp} - 2$.

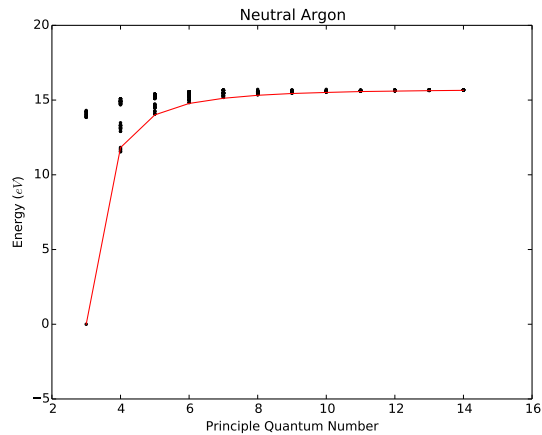


FIG. 1. Energy levels of neutral argon as a function of principle quantum number. Experiment (circles⁸). Hydrogenic energy level approximation (red line).

Figure 1 shows that energy level calculations for hydrogenic neutral argon are in good agreement with experimental data⁸, particularly so at larger n . Figure 1 also shows minimal variance in the energy of neutral argon per quantum number, which we expect for a hydrogenic particle. We use this evidence to assert our claim that argon can be treated as hydrogenic to a reasonable degree of approximation at high temperature.

It follows from Bohr's model that the radius of hydrogen-like electron orbitals are determined by $a_n = a_0 n^2$, where a_0 is the first Bohr radius and n is the principle quantum number. To avoid overlap between quantum states of neighboring atoms we wish to exclude electron orbits whose radius is larger than half the average distance between particles. We assume that this distance, r_s , can be expressed using the Wigner-Seitz radius

$$r_s = \left(\frac{3M}{4\pi Z \rho N_A} \right)^{\frac{1}{3}} \quad (2)$$

where M is the molar mass, Z is the number of free electrons per atom, ρ is the density, and N_A is Avogadro's number. Since we have chosen to terminate the internal partition function by using the principle quantum number, we must rearrange the equation for the classical Bohr radius so that n is isolated.

$$n_{cut} = \sqrt{r_s/r_b} = \left(\frac{1}{a_0} \right)^{\frac{1}{2}} \left(\frac{3M}{4\pi Z \rho N_A} \right)^{\frac{1}{6}} \quad (3)$$

Principle quantum numbers are defined such that for a quantum number n , $n \in \mathbb{N}^*$. It follows from Eq. 3 that if the quantum number $n = n_{cut}$ for a given orbital,

the radius of that orbital is exactly equal to half the average distance between particles, thus it should not be suppressed.

As can be seen from Eq. 2 the number of quantum states should decrease as the density, ρ increases. Figure 2 shows the dependence of the limiting quantum number on the density for neutral argon.

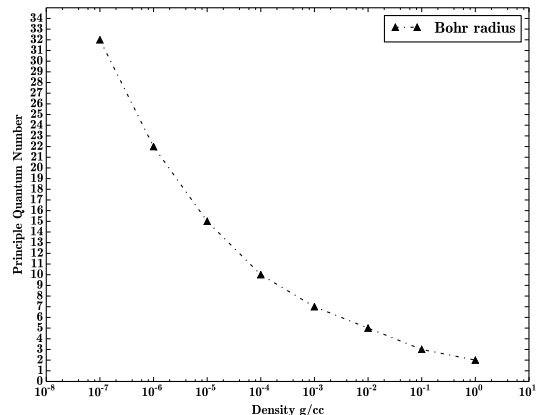


FIG. 2. Density dependence of the limiting quantum number for neutral argon. Density ranged from $\rho = 1 - 1 \times 10^{-7}$ to exhibit the decrease of available states as ρ increases.

B. Radial Wave Function Method

It is well known that the Bohr model, used in Section A., has significant shortcomings, particularly when it is applied to multi-electron atoms. Therefore, we modified the previously outlined method such that it relies upon more contemporary methods in quantum theory. This modification is outlined below.

It is easiest to solve the Schrödinger equation for hydrogen-like atoms in a spherically symmetric potential, as this is one of the few realistic systems whose analytic solution is well known. Thus, any simplification that allows us to model atoms or atomic ions as hydrogen-like is desirable. The wave functions for the hydrogen-like atom are defined by the principle quantum number n , the angular momentum quantum number l , and the magnetic quantum number m . We begin by writing the wave function as a product of a radial function and a spherical harmonic function.

$$\psi_{nlm} = R_{nl}(r)Y_l^m(\theta, \phi) \quad (4)$$

Where the radial function $R_{nl}(r)$ is written

$$R_{nl} = \sqrt{\left(\frac{2Z}{na_\mu} \right)^3 \frac{(n-l-1)!}{2n[(n-1)!]^3}} e^{-Zr/na_\mu} \left(\frac{2Zr}{na_\mu} \right)^l [L_{n-l-1}^{2l+1}(2Zr/na_\mu)] \quad (5)$$

Z is the atomic number. Since we have chosen to model neutral argon as hydrogenic ($Z = 1$), the atomic number

of an argon cation is taken to be $Z = 1 + q_+$, where q_+ is the cation's charge. Additionally we have introduced the value, $a_\mu = \frac{m_e}{\mu} a_0$, where m_e is the electron mass and μ is the reduced mass of the nucleus-electron system. Typically, the nucleus is much more massive than the electrons, so $\mu \approx m_e$ and it follows that $a_\mu = a_0$. In order to further simplify the problem, we have only considered S orbitals, thus $l = 0$ and $m = 0$. Under this assumption the spherical harmonics term, $Y_l^m(\theta, \phi)$ reduces to $\sqrt{\frac{1}{4\pi}}$. Thus, Eq. 4 becomes

$$\psi_{n00} = \sqrt{\frac{2}{\pi} \left(\frac{Z}{na_\mu}\right)^3 \frac{1}{2n[(n-1)!]^2}} e^{-Zr/na_\mu} [L_{n-1}^1(2Zr/na_\mu)] \quad (6)$$

We are then left to deal with the associated Laguerre polynomials, which are of the form

$$L_{q-p}^p = (-1)^p \left(\frac{d}{dx}\right)^p L_q(x) \quad (7)$$

where $L_q(x)$ is the q th Laguerre polynomial expressed as

$$L_q(x) = e^x \left(\frac{d}{dx}\right)^q (e^{-x} x^q) \quad (8)$$

and for the normalized hydrogen-like wavefunctions, $x = \frac{2Zr}{na_\mu}$.

The probability per unit volume of finding the electron at a point is equal to the square of the normalized wavefunction

$$\rho(r) = |\psi(r)_{n00}|^2 \quad (9)$$

It follows that the integral over all space of the radial probability density is written as

$$\int_0^\infty |\psi(r)_{n00}|^2 4\pi r^2 dr \quad (10)$$

More significantly, we may write the radial distribution function as

$$D(r) = |\psi(r)_{n00}|^2 4\pi r^2 \quad (11)$$

which represents the probability that an electron will be found in the infinitesimally small shell between r and $r + dr$. The normalized radial distribution function is then integrated in order to find the expectation value of the radius.

$$\langle r \rangle = \int_0^\infty r D(r) dr \quad (12)$$

If the expectation value of the radius for the given RDF exceeds the Wigner-Seitz radius, then the associated state is eliminated from the electronic partition function. In this work, the radial distribution function

was numerically integrated using an adaptive quadrature algorithm.

Figure 3 shows the limiting quantum number as a function of the density for the two methods. At $\rho = 10^0$ both methods for truncating the internal partition function converge to the same solution for neutral argon. At much smaller densities, there is a notable difference in the limiting quantum determined by the two methods. We expect this difference to be reflected in the equilibrium composition and EOS properties of the argon plasma.

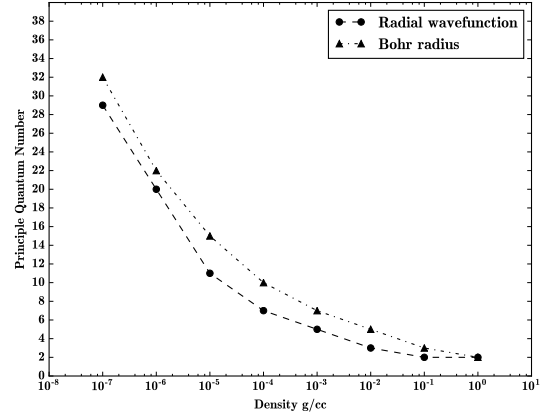


FIG. 3. Density dependence of the limiting quantum number for neutral argon. Both methods used for the truncation of the internal partition function are shown.

III. RESULTS

In this report we have used MAGPIE, a LANL HE-EOS code, to determine equilibrium composition and EOS properties for the argon plasma. EOS quantities are also reported for nitrogen as an ideal gas. Since nitrogen is not hydrogenic, the method described in Section II A must be modified significantly. For the purposes of this report we have calculated the radial functions of nitrogen as

$$P_{nl}(r) = \sum_{j=1}^k C_{jnl} N_{jnl} r^{I_{jnl}} e^{-\zeta_{jnl} r} \quad (13)$$

where N_{jnl} is the normalization factor

$$N_{jnl} = \frac{[2\zeta_{jnl}]^{I_{jnl}+1/2}}{[(2I_{jnl})!]^{1/2}} \quad (14)$$

The analytic form of the radial wavefunction was initially given by Hibbert et al.⁶ along with the parameters C_{jnl} , I_{jnl} , and ζ_{jnl} for $nl = 1s, 2s, 3s, 4s, 5s, 2p, 3p, 4p, 3d, 4d, 5d, 4f, 5f, 5g$. As we will elaborate upon later, this is all that is needed for our calculation of neutral nitrogen.

A. Argon Plasma

Limiting quantum numbers were calculated using the two methods described above and then were used as cutoff values for the internal partition functions of argon and its first and second cations. EOS properties and equilibrium compositions were calculated at densities of $\rho = 0.01$ g/cc & $\rho = 2.25$ g/cc. Temperatures ranged from $T=5,000$ K to $T= 200,000$ K in increments of 1,000 K. Our results are compared to the unbounded internal partition function, which we have defined as the partition function calculated using all NIST states below the first ionization energy of a given neutral particle or cation. At $\rho = 2.25$ g/cc the ground state method and the Bohr radius method return an identical value for the limiting quantum number, thus corresponding figures only include comparisons between EOS properties and compositions calculated using the radial wave function method, the ground state method, and the unbounded internal partition function.

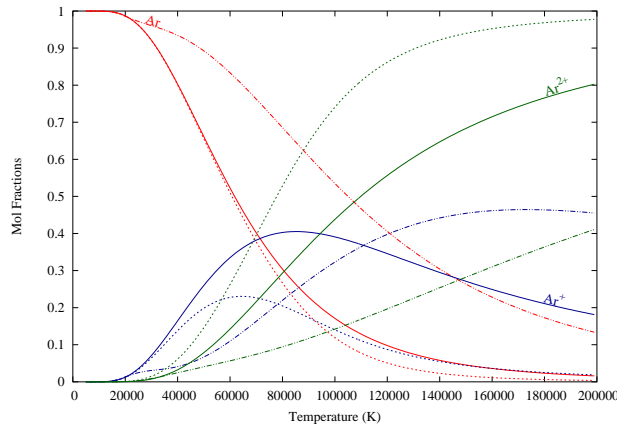


FIG. 4. Composition of the argon plasma at 2.25 g/cc. Three methods of truncating the partition function are shown. Ground State (solid line). Uncorrected (dash/dot). Radial Wave Function (dashed line).

Figure 4 serves as a demonstration of the unusual behavior that arises from the use of the unbounded internal partition function. Particularly, we see that in the case of the unbounded internal partition function the amount of Ar^{2+} never exceeds the amount of Ar^{+} present in the equilibrium composition. Corrected methods of calculating the internal partition function predict this transition to happen around $T=60,000$ K - $T=100,000$ K. While it is possible that this transition occurs outside of the temperature range presented in Figure 4, the temperature would be over 70% higher than the temperatures predicted by various cutoff methods. Even between corrected methods there is a marked difference in the temperature at

which this transition occurs. Furthermore, both Figure 4 and Figure 5 demonstrate that the specific method of truncating the electronic partition function will have an appreciable effect on the composition of the plasma above around $T = 20,000$ K. Since the doubly ionized ideal argon plasma is particularly sensitive to the cutoff value selected, it is the authors' opinion that subsequent discussions of EOS properties would be incomplete without mention of the cutoff method used.

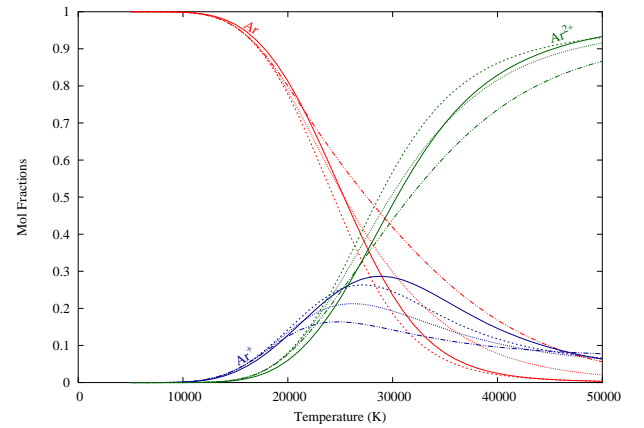


FIG. 5. Composition of the argon plasma at 0.01 g/cc. Three methods of truncating the partition function are shown. Ground State (solid line). Uncorrected (dash/dot). Radial Wave Function (dashed line). Bohr (dotted line).

EOS quantities that are affected by the internal partition function of neutral argon and its cations are shown in Figures 6-8.

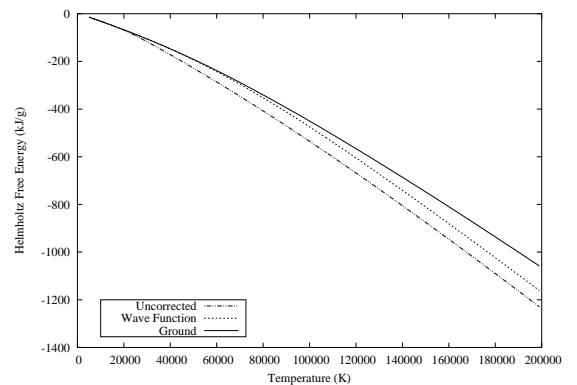


FIG. 6. Helmholtz free energy vs. T for the argon plasma at $\rho = 2.25$ g/cc

Figures 6-8 show that the EOS quantities affected by

the internal partition functions of argon and its cations also exhibit unusual behavior in the case of unbounded internal partition function. Particularly, Figures 7 and 8 show a sharp change in slope in the region from $T = 20,000$ K - $T = 40,000$ K. We believe this peculiarity to be due to the sudden thermal population of excited electronic states in argon that are inaccessible in the truncated partition functions of the other techniques.

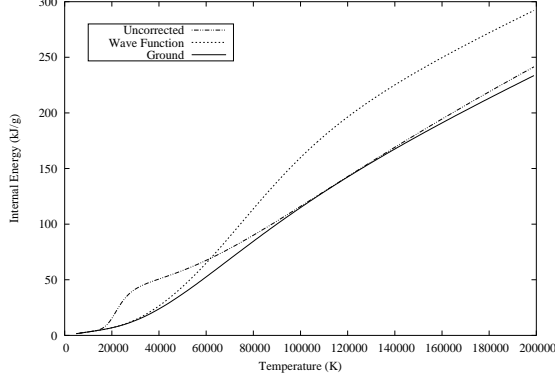


FIG. 7. Internal energy vs. T for the argon plasma at $\rho = 2.25$ g/cc

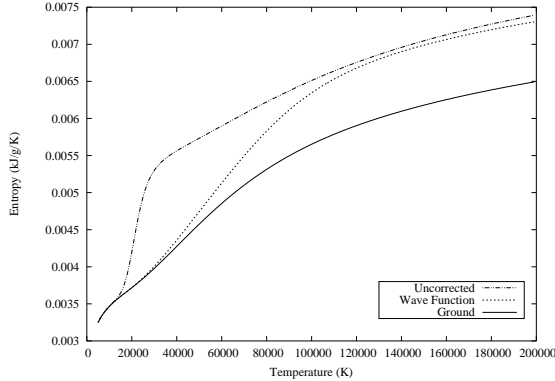


FIG. 8. Entropy vs. T for the argon plasma at $\rho = 2.25$ g/cc

B. Nitrogen Ideal Gas

It has already been stated that the nitrogen proves a more difficult problem. In the same manner as Figure 1, we have plotted energy level data for neutral nitrogen as reported by NIST⁸.

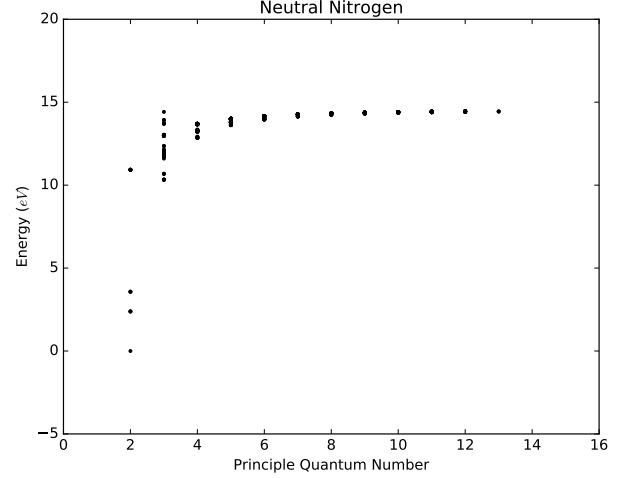


FIG. 9. Energy levels of neutral nitrogen as a function of principle quantum number. Data has been taken from the NIST Atomic Spectra Database⁸.

As demonstrated by Figure 9, there is a much greater variance in the energy of neutral nitrogen per principle quantum number than there was for neutral argon, particularly below $n = 4$. We have concluded that the variation in energy is too large to consider nitrogen as hydrogenic below the specified principle quantum number. Thus, the method outlined in Section II A becomes inapplicable.

Instead, we use the analytic form of the radial wave function⁶ to calculate radial distribution function for neutral nitrogen. Above $n = 4$, we consider neutral nitrogen as hydrogenic and thus we apply the Bohr method.

We have included the relevant EOS quantities calculated for neutral nitrogen as an ideal gas using our modified cutoff method. These results have been compared to the ground state method, and to a innate cutoff present in the MAGPIE code, based upon historically accepted values.

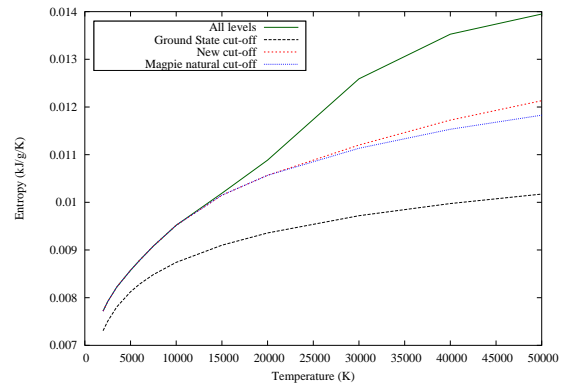


FIG. 10. Entropy vs. T for neutral nitrogen at $\rho = 2.25$ g/cc

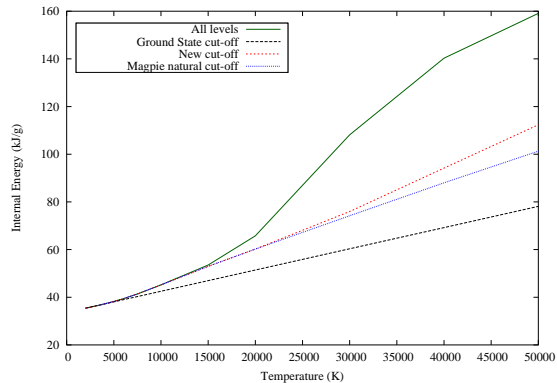


FIG. 11. Internal Energy vs. T for neutral nitrogen at $\rho = 2.25$ g/cc

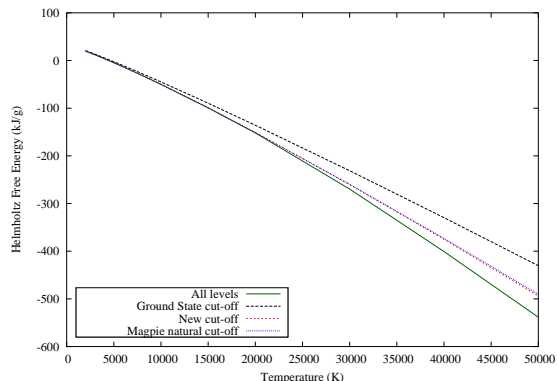


FIG. 12. Helmholtz free energy vs. T for neutral nitrogen at $\rho = 2.25$ g/cc

Figures 10 and 11 demonstrate that entropy and internal energy will typically be larger in value when calculated using our modified method then when using the ground state method. This is simply due to the fact that this method includes more states, which become thermally

populated at high temperature, thereby increasing equilibrium entropy and energy, as well as increasing the value of Z_{elec} . It follows that the internal partition function calculated from our modified method should be smaller in value than the uncorrected internal partition function. Accordingly, our values should be bounded by EOS quantities calculated from the uncorrected partition function and the ground state method. Figures 10-12 confirm that the EOS quantities calculated by our modified method lie within these bounds.

IV. CONCLUSION

Like many authors before us, we have concluded that a cutoff criterion must be considered when calculating the internal partition function, particularly at high temperatures. Additionally, we assert that differences in the internal partition function have less of an effect on composition and EOS properties at low temperatures than they do at high temperatures. The validity of this claim falls out of the fact that the compositions, Helmholtz free energies, entropies, and internal energies (Figures 4-8) calculated from the internal partition functions used in our comparisons converge below $T = 10,000$ K for the argon plasma. While we do not see a similar convergence for the entropy of neutral nitrogen below $T = 10,000$ K, Figure 10 shows that the differences between methods are within 9% below $T = 10,000$ K and reach a maximum difference of 19% at $T = 50,000$ K. Thus, differences in the internal partition function appear to have a more appreciable effect as temperature increases.

A similar conclusion can be reached by examining the magnitude of the energy levels. For low temperatures only the first few terms make a substantial contribution to the internal partition function. Thus, the internal partition function can be described as self-limiting in this regime. At temperatures greater than $T = 20,000$ K we begin to see appreciable differences in the composition and EOS quantities calculated using various methods for determining the cutoff. Thus we conclude that in presenting these properties one must include their method for terminating the internal partition function.

Future work is expected to include EOS quantities of the nitrogen plasma using methods outlined in this study. At high densities, we expect this to include the accurate calculation of wavefunctions for nitrogen and its ions.

¹ H. N. Olsen. Partition function cutoff and lowering of the ionization potential in an argon plasma. *Phys. Rev.*, 124: 1703–1708, Dec 1961. doi:10.1103/PhysRev.124.1703. URL <https://link.aps.org/doi/10.1103/PhysRev.124.1703>.

² K. S. Drellishak, C. F. Knopp, and Ali Bulent Cambel. Partition functions and thermodynamic properties of argon plasma. *The Physics of Fluids*, 6(9):1280–1288, 1963. doi: 10.1063/1.1706896. URL <https://aip.scitation.org/doi/abs/10.1063/1.1706896>.

³ John W. Bond. Structure of a shock front in ar-

gon. *Phys. Rev.*, 105:1683–1694, Mar 1957. doi: 10.1103/PhysRev.105.1683. URL <https://link.aps.org/doi/10.1103/PhysRev.105.1683>.

⁴ W. Ecker, G. ; Weizel. Partial function and effective ionization potential of the atoms of interior of plasmas. *Ann. Physik*, 17, 1957.

⁵ D. G. Hummer and D. Mihalas. The equation of state for stellar envelopes. I - an occupation probability formalism for the truncation of internal partition functions. *Astrophys. J.*, 331:794–814, August 1988. doi:10.1086/166600.

- ⁶ A. Hibbert, E. Biemont, M. Godefroid, and N. Vaeck. New accurate transition probabilities for astrophysically important spectral lines of neutral nitrogen. , 88:505–524, June 1991.
- ⁷ Hans R. Griem. *Plasma Spectroscopy*. McGraw-Hill, 1964.
- ⁸ A. Kramida, Yu. Ralchenko, J. Reader, and and NIST ASD Team. NIST Atomic Spectra Database (ver. 5.5.6), [Online]. Available: <https://physics.nist.gov/asd> [2017, April 9]. National Institute of Standards and Technology, Gaithersburg, MD., 2018.